Determination of the Electron Affinity Energy of Antimony and Bismuth Atoms by a Surface-Ionization Method Applicable to Elements with a Complex Vapor Composition

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Abstract

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E. Ya. Zandberg, V. I. Paleev

Determination of the Electron Affinity Energy of Antimony and Bismuth Atoms by a Surface-Ionization Method Applicable to Elements with a Complex Vapor Composition

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The affinity of atoms for an electron, S, can be determined by several methods based on the use of surface ionization (^{1}). These methods assume that the fluxes of particles ionized at the emitter consist either of atoms or of molecules that dissociate completely into atoms on the emitter. The most reliable determinations of S have been made by methods that do not require measurement of the emitter work function: by comparing the temperature dependences of the thermoelectron current and the current of negative ions, or the currents of negative ions of two simultaneously ionized elements satisfying the condition:

$$e(\varphi_{\min} - S - \sqrt{e\mathcal{E}}) \gg kT \tag{1}$$

(e is the charge; $\varphi_{\min}$ is the minimum value of the work function of an inhomogeneous emitter; $\mathcal{E}$ is the intensity of the electric field at the emitter, which draws electrons and ions into the vacuum; k is Boltzmann' s constant; T is the emitter temperature).

In the first method, the following relation is used to determine S:

$$\ln \frac{i_{\mathrm{e}}}{i\_T^2} = B - \frac{eS}{kT}, \tag{2}$$

where i_{e} is the thermoelectron current; $i\_$ is the negative-ion current, and B is a quantity independent of T, which also includes the constant flux of atoms to the emitter, v.

In the second method, the relation used is

$$\ln \frac{i_{-1}}{i_{-2}} = \ln \frac{v_1 Q_1}{v_2 Q_2} + \frac{e}{kT}(S_1 - S_2), \tag{3}$$

where Q denotes the ratios of the statistical sums Q_-/Q_0 of the possible states of negative ions and atoms; the indices 1 and 2 refer to different elements. From the value of the difference $(S_1 - S_2)$ and the known affinity of the element chosen for comparison, the unknown S of the second element is determined.

The first method is used in the magnetron technique for determining S ([2]); by the second method the affinity of halogens, sulfur, copper, silver, and gold has been determined ([3–5]).

Neither of these methods can be used in the case of elements with a complex vapor composition, the degree of dissociation of whose molecules on the emitter depends on temperature (for example, in the case of antimony ([6,7]) and bismuth ([6,7])). Indeed, in the mass spectra of surface ionization of Sb on tungsten we observed currents of ions Sb^-, Sb_2^-, and Sb_3^-, and in the mass spectrum of bismuth, currents of ions Bi^-, Bi_2^-, and traces of Bi_3^-.

The affinity of atoms of elements with a complex vapor composition can be determined by comparing the currents of atomic negative and positive ions formed by surface ionization, provided that these currents are measurable quantities.

Let us consider ionization on a nonuniform surface, adopting a sharp patch scheme with different work functions φ_i on the emitter and assuming the contact field of the patches to be compensated by an external electric field ([1]). Under these conditions the ion currents of difficult-to-ionize elements are

$$i_- = e\nu K_- \frac{Q_-}{Q_0} \sum_i F_i \exp \frac{e}{kT} \left(S + \sqrt{e\mathcal{E}} - \varphi_i\right), \tag{4}$$

$$i_+ = e\nu K_+ \frac{Q_+}{Q_-} \sum_i F_i \exp \frac{e}{kT} \left(\varphi_i + \sqrt{e\mathcal{E}} - V\right). \tag{5}$$

In (4) and (5), F_i is the area of the patches with work function φ_i, and K_- and K_+ are coefficients that include the transmission coefficients of ions of different charge and mass in the mass spectrometer and the corresponding coefficients of multiplication by the multiplier in the receiver of the instrument.* The flux of ionized atoms ν includes the atomic flux incident on the surface and the atoms formed on the emitter as a result of dissociation of molecular fluxes.

If two elements are ionized simultaneously and a comparison of the ratios i_-/i_+ is made, then the unknown quantities φ_i and F_i entering the sums (4) and (5) are eliminated, and the difference $S_1 - S_2$ can be found, since

$$\left(\frac{i_-}{i_+}\right)_1 \left(\frac{i_+}{i_-}\right)_2 = \left(\frac{Q_-}{Q_+}\right)_1 \left(\frac{Q_+}{Q_-}\right)_2 \left(\frac{K_-}{K_+}\right)_1 \left(\frac{K_+}{K_-}\right)_2 \exp \frac{e}{kT} \left(S_1 - S_2 + V_1 - V_2\right), \tag{6}$$

and all the other quantities in (6) can be determined. The accuracy of measuring the unknown quantity S depends, as in any comparison method, not only on the accuracy of measuring the difference $(S_1 - S_2)$, but also on the accuracy with which S of the reference element has been determined.

It can be shown that formula (6) is also valid in the absence of compensation of the contact field of the patches.

In the measurements of S_{Sb} and S_{Bi}, silver was the reference element; $S_{\mathrm{Ag}} = 2.0 + 0.2$ eV was determined by comparison with iodine in ([5]).

A mass-spectrometric apparatus ([9]) was used, with two simultaneously operating evaporators and an emitter—a tungsten wire of diameter $\phi = 200\,\mu$. The ion receiver device with a multiplier for measuring currents of positive and negative ions of equal energy in metal systems was reported in ([10]). The ion energy was 1100 eV; saturation currents were measured. The residual pressure in the instrument during measurements of positive-ion currents was $\sim 3 \cdot 10^{-7}$ torr and increased to $1 \cdot 10^{-6}$ torr owing to electron-stimulated desorption from the electrodes during measurements of negative-ion currents. It can be shown that the vacuum requirements when measuring currents in the method used are not stringent if condition (1) is not violated and the condition $e(V - \varphi_{\max} - \sqrt{e\mathcal{E}}) \gg kT$ is satisfied. Ion currents were measured at a constant emitter temperature T (within 2300-2500° K) in the sequence $(i_-)_1$, $(i_-)_2$, $(i_+)_2$, $(i_+)_1$, $(i_-)_1$, $(i_-)_2$.

In calculating the differences $(S_1 - S_2)$ from (6), the following values were adopted: $V_{\mathrm{Sb}} = 8.64$ V, $V_{\mathrm{Bi}} = 7.29$ V, $V_{\mathrm{Ag}} = 7.57$ V. The statistical sums Q_- and Q_+ were replaced by the statistical weights g of the ground states of the ions, since excited states of negative ions are unlikely ([11]), and the excitation energy of the nearest levels of the positive ions Sb^+, Bi^+, and Ag^+ is large in comparison with kT ([12]). For silver $g_+/g_- = 1$; for Sb and Bi $g_+/g_- = 1/5$. It was assumed that $(K_-/K_+)_1(K_+/K_-)_2 = 1$, which, according to estimates of the secondary-emission coefficients at the first dynode of the multiplier ([13,14])

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* The use of mass-spectrometric technique for separate measurement of ion currents is assumed.

can lead to a systematic error in the determinations of $(S_1 - S_2)$ of less than 0.2 V.

From many determinations the following values of the differences $(S_1 - S_2)$ were found:

$$S_{\mathrm{Ag}} - S_{\mathrm{Sb}} = (0.40 \pm 0.07)\ \mathrm{V}; \qquad S_{\mathrm{Ag}} - S_{\mathrm{Bi}} = (0.14 \pm 0.06)\ \mathrm{V}.$$

Here and in the subsequent determinations the root-mean-square errors are given.

Fig. 1

Figure 1: Fig. 1

The values of the differences ($S_1 - S_2$) are only weakly sensitive to errors in temperature measurement: thus, for $\Delta T = \pm 100^\circ$ for antimony, $\Delta S_{\mathrm{Sb}} \simeq \pm 0.05$ V.

We also measured the value S_{Ag} by comparing the temperature dependences of the thermoelectron and ion currents, replacing one of the evaporators by an electron collector. Figure 1 shows a typical plot of dependence (2) for silver. From many measurements there was obtained

$$S_{\mathrm{Ag}} = (1.90 \pm 0.15)\ \mathrm{V},$$

which agrees, within the experimental errors, with the value obtained in (5) by another method. Thus,

$$S_{\mathrm{Sb}} = (1.50 \pm 0.17)\ \mathrm{V},$$

$$S_{\mathrm{Bi}} = (1.76 \pm 0.16)\ \mathrm{V}.$$

Fig. 1

In the literature there are only rough estimates of these quantities ($S_{\mathrm{Sb}} \gtrsim 2$ V, $S_{\mathrm{Bi}} > 0.7$ V (^{6})).

By the method of comparing the currents of positive and negative ions of two elements, we also attempted to estimate the electron affinity of indium atoms. The current of In^- ions at the largest particle flux densities from the evaporator possible in the experiments was only at the limit of measurability. It is evident that $S_{\mathrm{In}} \ll S_{\mathrm{Sb}}$; the estimates give

$$S_{\mathrm{In}} \approx (0.8 \div 1.1)\ \mathrm{V}.$$

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Ioffe Physico-Technical Institute
Academy of Sciences of the USSR
Leningrad

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Note: Figure translations are in progress. See original paper for figures.